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(51) International Patent Classification ⁷ : C08F 4/603, 4/02, 10/00	A1	(11) International Publication Number: WO 00/04059 (43) International Publication Date: 27 January 2000 (27.01.00)
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(54) Title: SUPPORTED LEWIS ACID COCATALYSTS FOR OLEFIN POLYMERIZATION (57) Abstract The invention relates to an olefin polymerization catalyst which is the reaction product of 1) transition metal compounds having ancillary, stabilizing ligands and at least two labile ligands suitable for insertion of olefins and capable of abstraction or removal so as to form active cationic transition metal centers and 2) a support bound Lewis acid comprising a boron atom having two halogenated aryl ligands and a third ligand being a heteroatom covalently bonded to a polymeric or metal/metalloid oxide support. Olefin polymerization with certain embodiments are illustrated. The invention includes a process for the polymerization of olefinically unsaturated monomers comprising contacting a plurality of one or more of said monomers with the invention catalyst.		

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TITLE: SUPPORTED LEWIS ACID COCATALYSTS FOR OLEFIN
POLYMERIZATION

5

TECHNICAL FIELD

This invention relates to the supported ionic catalyst systems based on transition metal compounds activated by aryl-group containing Lewis acids that are capable of providing insertion polymerization catalysts and to the preparation of olefin polymers.

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BACKGROUND OF THE INVENTION

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Group 13 based Lewis acids having fluorinated aryl substituents are known to be capable of activating transition metal compounds into olefin polymerization catalysts. Tris(perfluorophenyl)borane is demonstrated in EP 0 425 697 and EP 0 520 732 to be capable of ionizing cyclopentadienyl derivatives of transition metals by abstracting a ligand and providing a stabilizing, compatible noncoordinating anion. See also, Marks, *et al*, J. Am. Chem. Soc. 1991, 113, 3623-3625. The term "noncoordinating anion" is now accepted terminology in the field of olefin polymerization, both by coordination or insertion polymerization and carbocationic polymerization. See, for example, EP 0 277 004, U.S. patent 5,198,401, and Baird, Michael C., *et al*, J. Am. Chem. Soc. 1994, 116, 6435-6436, and U.S. patent 5,668,324. The noncoordinating anions are described to function as electronic stabilizing cocatalysts, or counterions, for cationic metallocene complexes which are active for olefin polymerization. The term noncoordinating anion as used here applies both to truly noncoordinating anions and coordinating anions that are at most weakly coordinated to the cationic complexes so as to be labile to replacement by olefinically or acetylenically unsaturated monomers. Thus the use of ionic catalysts for olefin polymerization where organometallic transition metal cations are stabilized in an active polymerization state by compatible, non-coordinating

anions is a well-recognized field in the chemical arts. Typically such organometallic transition metal cations are the chemical derivatives of organometallic transition metal compounds having both ancillary ligands which help stabilize the compound in an active electropositive state and labile ligands at least one of which can be abstracted to render the compound cationic and at least one of which is suitable for olefin insertion. Since inert supports are used industrially for insertion polymerization processes in both of gas phase polymerization and slurry polymerization, technology for supporting these ionic catalysts is also known.

Supported non-coordinating anions derived from tris(perfluorophenyl) boron are described in U.S. patent 5,427,991. The tris(perfluorophenyl) boron is shown to be capable of reacting with coupling groups bound to silica through hydroxyl groups to form support bound anionic activators capable of activating transition metal catalyst compounds by ligand abstraction. U.S. patent 5,643,847 discusses the reaction of Group 13 Lewis acid compounds with metal/metalloid oxides such as silica. It illustrates the reaction of tris(perfluorophenyl) boron with silanol groups so as to prepare bound anion precursors capable of ionizing, by protonation, transition metal organometallic compounds and forming catalytically active cations counter-balanced by bound anions.

Immobilized Lewis acid catalysts suitable for carbocationic polymerization are described in U.S. patent 5,288,677. The Group III A Lewis acids of the invention are said to have the general formula R_nMX_{3-n} where M is a Group III A metal, R is a monovalent hydrocarbon radical consisting of C_1 to C_{12} alkyl, aryl, alkylaryl, arylalkyl and cycloalkyl radicals, $n = 0 - 3$, and X is halogen. Listed Lewis acids include aluminum trichloride, trialkyl aluminums, and alkylaluminum halides. Immobilization is accomplished by reacting the invention Lewis acids with hydroxyl, halide, amine, alkoxy, secondary alkyl amines, and others, where the groups are structurally incorporated in a polymeric chain. James C.W. Chien, Jour. Poly. Sci.: Pt A: Poly. Chem, Vol. 29, 1603 - 1607 (1991), has described the olefin polymerization utility of methylalumoxane (MAO) reacted with SiO_2 and zirconocenes. He proposes a covalent bonding of the aluminum atom to the silica

through an oxygen atom in surface hydroxyl groups. Each of the documents of the foregoing paragraphs are incorporated by reference for purposes of U.S. patent practice.

5 In view of the above there is a continuing need for activating cocatalyst compounds both to improve industrial economics and to provide simpler methods of synthesis and preparation of suitable activating compounds for ionic catalyst systems. Additionally, improvements in gas phase and slurry polymerization of olefins, where supported catalysts are typically used, are sought so as to meet the demanding criteria of industrial processes. The complexities of the polymerization media of industrial processes
10 can result in widely varying product properties of the polymers prepared and the polymer particles formed in the reactors from which the polymerization medium must be removed for final product preparation.

SUMMARY OF THE INVENTION

15 This invention addresses transition metal organometallic catalyst compounds comprising the reaction product of a suitable transition metal organometallic compound and a support bound bisaryl boron compound wherein both aryl ligands are halogenated, and processes for the preparation of polyolefins from one or more olefinic monomers
20 comprising combining said olefins with this transition metal organometallic catalyst compound.

DESCRIPTION OF THE INVENTION

25 The invention provides an olefin polymerization catalyst which is the reaction product of 1) transition metal compounds having ancillary, stabilizing ligands and at least two labile ligands suitable for insertion of olefins and capable of abstraction or removal so as to form active cationic transition metal centers and 2) a support bound, neutral Lewis acid comprising a boron atom having two halogenated aryl ligands and a third ligand
30 which is a heteroatom covalently bonded to a polymeric or metal/metalloid oxide

support. These Lewis acid activators and the organometallic catalyst precursor compounds combine to form active ionic catalysts for olefin polymerization by ligand abstraction. The invention includes a suitable method for preparing polymers and copolymers of two or more monomers by contacting the active catalyst with insertion
5 polymerizable monomers, those having accessible olefinic unsaturation.

Lewis acid compounds of the invention are those olefin catalyst activator Lewis acids based on boron metalloid centers and having two bulky, electron-withdrawing ligands such as the halogenated aryl ligands of tris(perfluorophenyl)borane. These bulky
10 ligands should be those sufficient to allow the Lewis acids to function as electronically stabilizing, compatible noncoordinating anions. Stable ionic complexes are achieved when the anions are not readily hydrolyzed and will not be a suitable ligand donor to the strongly Lewis acidic cationic organometallic transition metal cations used in insertion polymerization, i.e., inhibit ligand transfer that would neutralize the cations and render
15 them inactive for polymerization. The Lewis acids fitting this description can be described by the following formula:



where R is a monoanionic ligand, B is boron and ArHal is a halogenated C₆ aromatic or
20 higher carbon number polycyclic aromatic hydrocarbon or aromatic ring assembly in which two or more rings (or fused ring systems) are joined directly to one another or together. Suitable R ligands include: hydride; substituted or unsubstituted C₁ to C₃₀ hydrocarbyl aliphatic or aromatic groups, substituted meaning that at least one hydrogen on a carbon atom is replaced with a hydrocarbyl, halide, halocarbyl, hydrocarbyl or
25 halocarbyl substituted organometalloid, dialkylamido, alkoxy, aryloxy, alkylsulfido, arylsulfido, alkylphosphido, alkylphosphido or other anionic substituent; fluoride; bulky alkoxides, where bulky refers to C₄ and higher number hydrocarbyl groups, e.g., up to about C₂₀, such as tert-butoxide and 2,6-dimethylphenoxide, and 2,6-di(tert-butyl)phenoxide; -SR; -NR₂, and -PR₂, where each R is independently a substituted or

unsubstituted hydrocarbyl as defined above; and, C_1 to C_{30} hydrocarbyl substituted organometalloid, such as trimethylsilyl. Examples of ArHal include the phenyl, naphthyl and anthracenyl radicals of U.S. patent 5,198,401 and the biphenyl radicals of WO 97/29845, preferably when a majority of fused-ring hydrogen atoms are replaced with halogens. The generic use of the terms halogenated or halogenation means for the purposes of this application that at least one third of hydrogen atoms on carbon atoms of the aryl-substituted aromatic ligands be replaced by halogen atoms, and more preferred that the aromatic ligands be of sufficient molecular size to partially inhibit or help to prevent neutralization of the invention transition metal cation by Lewis bases other than the polymerizable monomers that may be present in the polymerization process. Suitable noncoordinating anions are described in U.S. patents 5,198,401, 5,278,119, 5,407,884, 5,599,761. All documents are incorporated by reference for purposes of U.S. patent practice.

Lewis acidic bisaryl boron compounds according to the above formula can be prepared or synthesized in accordance with methods known in the art. In particular, methods of preparing $(C_6F_5)_2BH$ are specifically taught in U.S. patent 5,496,960. Generally, the starting material is the Lewis acidic chlorine analog, $(C_6F_5)_2BCl$, and reaction with less Lewis acidic organometallic/metalloid compounds, e.g., $ClHSiMe_2$ or $(Bu)_3SnD$ (where Bu is butyl and Me is methyl), was reported to yield the hydride or deuteride products respectively. In a similar manner, replacing the H or D group in the Lewis acidic organometallic/metalloid compounds with another anionic ligand according to the definition of R above, can be utilized to prepare other suitable Lewis acidic bisaryl boron compounds according to this description. Replacing the C_6F_5 groups on $(C_6F_5)_2BCl$ with other halogenated aryl groups permits the preparation of invention compounds with the full range of supported neutral Lewis acid compounds suitable as cocatalyst activators and sources of the support bonded, discrete noncoordinating anions.

The term noncoordinating anion as used for the invention compounds is art recognized to mean an anion which either does not coordinate to said transition metal

cation or which is only weakly coordinated to said cation thereby remaining sufficiently labile to be displaced by a neutral Lewis base. "Compatible" noncoordinating anions are those which are not degraded to neutrality when the complexes between them and the transition-metal cationic catalyst compounds are formed. Further, the anion will not transfer an anionic substituent or fragment to the cation so as to cause it to form a neutral four coordinate metal compound and a neutral by-product from the anion. Noncoordinating anions useful in accordance with this invention are those which are compatible, stabilize the invention transition metal cation in the sense of balancing its ionic charge, yet retain sufficient lability to permit displacement by an olefinically unsaturated monomer during polymerization. Additionally, being support bonded, the anions useful in this invention will be of sufficient molecular size to partially inhibit or help to prevent neutralization of the invention transition-metal cation by Lewis bases other than the polymerizable monomers that may be present in the polymerization process. Suitable aryl ligands for the invention include those of the noncoordinating anions are described in U.S. patents 5,198,401, 5,278,119, 5,407,884, 5,599,761. All documents are incorporated by reference for purposes of U.S. patent practice.

The metal or metalloid oxide supports of the invention include any metal/metalloid oxides having surface hydroxyl groups exhibiting a pK_a equal to or less than that observed for amorphous silica, i.e., pK_a less than or equal to about 11. In forming the invention covalently bound anionic activator the Lewis acid is believed to form initially a dative complex with a silanol group (which acts as a Lewis base) thus forming a formally dipolar (zwitterionic) Bronsted acid structure bound to the metal/metalloid of the metal oxide support. Thereafter the proton of the Bronsted acid appears to protonate the R-group of the Lewis acid, abstracting it, at which time the Lewis acid becomes covalently bonded to the oxygen atom. The R group of the Lewis acid then becomes $R'-O-$, where R' is a suitable support substrate, e.g., silica. Accordingly any of the conventionally known silica support materials that retain hydroxyl groups after dehydration treatment methods will be suitable in accordance with the invention. Because of availability, both of silica and silica

containing metal oxide based supports, for example, silica-alumina, are preferred. Silica particles, gels and glass beads are most typical.

These metal oxide compositions may additionally contain oxides of other metals, such as those of Al, K, Mg, Na, Si, Ti and Zr and should preferably be treated by thermal and/or chemical means to remove water and free oxygen. Typically such treatment is in a vacuum in a heated oven, in a heated fluidized bed or with dehydrating agents such as organo silanes, siloxanes, alkyl aluminum compounds, etc. The level of treatment should be such that as much retained moisture and oxygen as is possible is removed, but that a chemically significant amount of hydroxyl functionality is retained. Thus calcining at up to 800 °C, or more up to a point prior to decomposition of the support material, for several hours is permissible, and if higher loading of supported anionic activator is desired, lower calcining temperatures for lesser times will be suitable. Where the metal oxide is silica, loadings to achieve from less than 0.1 mmol to 3.0 mmol activator/g SiO₂ are typically suitable and can be achieved, for example, by varying the temperature of calcining from 200 to 800+ °C. See Zhuralev, *et al*, Langmuir 1987, vol. 3, 316 where correlation between calcining temperature and times and hydroxyl contents of silicas of varying surface areas is described.

The tailoring of hydroxyl groups available as attachment sites in this invention can also be accomplished by the pre-treatment, prior to addition of the Lewis acid, with a less than stoichiometric amount of the chemical dehydrating agents. Preferably those used will be used sparingly and will be those having a single ligand reactive with the silanol groups (e.g., (CH₃)₄SiCl), or otherwise hydrolyzable, so as to minimize interference with the reaction of the transition metal catalyst compounds with the bound activator. If calcining temperatures below 400 °C are employed, difunctional coupling agents (e.g., (CH₃)₃SiCl₂) may be employed to cap hydrogen bonded pairs of silanol groups which are present under the less severe calcining conditions. See, e.g., "Investigation of Quantitative SiOH Determination by the Silane Treatment of Disperse Silica", Gorski, *et al*, Journ. of

Colloid and Interface Science, Vol. 126, No. 2, Dec. 1988, for discussion of the effect of silane coupling agents for silica polymeric fillers that will also be effective for modification of silanol groups on the catalyst supports of this invention. Similarly, use of the Lewis acid compounds of the invention in excess of the stoichiometric amount needed for reaction with the transition metal compounds will serve to neutralize excess silanol groups without significant detrimental effect for catalyst preparation or subsequent polymerization.

Polymeric supports are preferably hydroxyl-functional-group-containing polymeric substrates, but may be any of the primary alkyl amines, secondary alkyl amines, and others, where the groups are structurally incorporated in a polymeric chain and capable of an acid-base reaction with the Lewis acid such that a ligand filling one coordination site of the boron is protonated and replaced by the polymer incorporated functionality. See, for example, the polymers of U.S. patent 5,288,677, the teachings of which are incorporated by reference for purposes of U.S. patent practice. In accordance with these teachings, preferred heteroatoms constituting the third ligand of the bisaryl boron compounds of the invention, will be Group 15 or 16 heteroatoms, most preferably oxygen or nitrogen.

Organometallic transition metal compounds suitable as olefin polymerization catalysts by coordination or insertion polymerization in accordance with the invention will include the known transition metal compounds useful in traditional Ziegler-Natta coordination polymerization and as well the metallocene compounds similarly known to be useful in coordination polymerization, when such compounds are capable of catalytic activation by the cocatalyst activators described for the invention. These will typically include Group 3-10 transition metal compounds having bulky ancillary ligands not prone to abstraction and two labile metal ligands which can be abstracted by the cocatalyst activators. Labile ligands include hydrocarbyl ligands, such as hydride or alkyl, and hydrocarbylsilyl, such as trimethylsilyl. Ligands capable of abstraction and transition metal compounds comprising them include those described in the background art, see for

example US patents 5,198,401 and 5,278,119. Syntheses of these compounds are well known from the published literature. Additionally, where the metal ligands include halogen, amido or alkoxy moieties (for example, biscyclopentadienyl zirconium dichloride) which are not capable of abstraction with the activating cocatalysts of the invention, they can be converted via known alkylation reactions with organometallic compounds such as lithium or aluminum hydrides or alkyls, alkylalumoxanes, Grignard reagents, etc. See also EP-A1-0 570 982 for the reaction of organoaluminum compounds with dihalo-substituted metallocene compounds prior to addition of activating anion compounds. All documents are incorporated by reference for purposes of U.S. patent practice.

Additional description of metallocene compounds which comprise, or can be alkylated to comprise, at least one ligand capable of abstraction to form a catalytically active transition metal cation appear in the patent literature, for example EP-A-0 129 368, US patents 4,871,705, 4,937,299, 5,324,800 EP-A- 0- 418 044, EP-A-0 591 756, WO-A-92/00333 and WO-A-94/01471. Such metallocene compounds can be described for this invention as mono- or biscyclopentadienyl substituted Group 3, 4, 5, 6, 9, or 10 transition metal compounds wherein the ancillary ligands may be themselves substituted with one or more groups and may be bridged to each other, or may be bridged through a heteroatom to the transition metal. The size and constituency of the ancillary ligands and bridging elements are not critical to the preparation of the ionic catalyst systems of the invention but should be selected in the literature described manner to enhance the polymerization activity and polymer characteristics being sought. Preferably the cyclopentadienyl rings (including substituted cyclopentadienyl-based fused ring systems, such as indenyl, fluorenyl, azulenyl, or substituted analogs of them), when bridged to each other, will be lower alkyl-substituted (C_1 - C_6) in the 2 position (without or without a similar 4-position substituent in the fused ring systems) and may additionally comprise alkyl, cycloalkyl, aryl, alkylaryl and or arylalkyl substituents, the latter as linear, branched or cyclic structures including multi-ring structures, for example, those of U.S. patents 5,278,264 and 5,304,614. Such substituents should each have essentially hydrocarbyl

characteristics and will typically contain up to 30 carbon atoms but may be hetero-atom containing with 1-5 non-hydrogen/carbon atoms, e.g., N, S, O, P, Ge, B and Si. All documents are incorporated by reference for purposes of U.S. patent practice.

5 Metallocene compounds suitable for the preparation of linear polyethylene or ethylene-containing copolymers (where copolymer means comprising at least two different monomers) are essentially any of those known in the art, see again EP-A-277,004, WO-A-92/00333 and U.S. patents 5,001,205, 5,198,401, 5,304,614, 5,308,816, and 5,324,800 for specific listings. Selection of metallocene compounds for use to make
10 isotactic or syndiotactic polypropylene, and their syntheses, are well-known in the art, specific reference may be made to both patent literature and academic, see for example Journal of Organometallic Chemistry 369, 359-370 (1989). Typically those catalysts are stereorigid asymmetric, chiral or bridged chiral metallocenes. See, for example, U.S. patent 4,892,851, U.S. patent 5,017,714, U.S. patent 5,296,434, U.S. patent 5,278,264,
15 WO-A-(PCT/US92/10066) WO-A-93/19103, EP-A2-0 577 581, EP-A1-0 578 838, and academic literature "The Influence of Aromatic Substituents on the Polymerization Behavior of Bridged Zirconocene Catalysts", Spaleck, W., et al, Organometallics 1994, 13, 954-963, and "ansa-Zirconocene Polymerization Catalysts with Annelated Ring Ligands-Effects on Catalytic Activity and Polymer Chain Lengths", Brinzinger, H., et al,
20 Organometallics 1994, 13, 964-970, and documents referred to therein. Though many above are directed to catalyst systems with alumoxane activators, the analogous metallocene compounds will be useful with the cocatalyst activators of this invention for active coordination catalyst systems, when the halogen, amide or alkoxy containing ligands of the metals (where occurring) are replaced with ligands capable of abstraction,
25 for example, via an alkylation reaction as described above, and another is a group into which the ethene group $-C=C-$ may insert, for example, hydride, alkyl, or silyl. All documents are incorporated by reference for purposes of U.S. patent practice.

30 Non-limiting representative metallocene compounds include monocyclopentadienyl compounds such as pentamethylcyclopentadienyltitanium isopropoxide,

pentamethylcyclopentadienyltribenzyl titanium,
 dimethylsilyltetramethylcyclopentadienyl-tert-butylamido titanium dichloride,
 pentamethylcyclopentadienyl titanium trimethyl,
 dimethylsilyltetramethylcyclopentadienyl-tert-butylamido zirconium dimethyl,
 5 dimethylsilyltetramethylcyclopentadienyl-dodecylamido hafnium dihydride,
 dimethylsilyltetramethylcyclopentadienyl-dodecylamido hafnium dimethyl, unbridged
 biscyclopentadienyl compounds such as bis(1,3-butyl, methylcyclopentadienyl) zirconium
 dimethyl, pentamethylcyclopentadienyl-cyclopentadienyl zirconium dimethyl,
 tetramethylcyclopentadienyl-n-propylcyclopentadienyl zirconium dimethyl, indenyl-
 10 cyclopentadienyl zirconium dimethyl; bridged biscyclopentadienyl compounds such as
 dimethylsilylbis(tetramethylcyclopentadienyl) (cyclopentadienyl) zirconium dichloride,
 silacyclobutyl(tetramethylcyclopentadienyl)(n-propyl-cyclopentadienyl)zirconium
 dichloride; bridged bisindenyl compounds such as dimethylsilylbisindenyl zirconium
 dichloride, dimethylsilylbisindenyl hafnium dimethyl, dimethylsilylbis(2-
 15 methylbenzindenyl) zirconium dichloride, dimethylsilylbis(2-methylbenzindenyl)
 zirconium dimethyl; bridged fluorenyl compounds such as
 diphenylmethylenefluorenyl(cyclopentadienyl)hafnium dimethyl, silacyclobutyl(1,7-di-
 tertbutylfluorenyl)(cyclopentadienyl)zirconium dichloride, isopropylidene-bis(fluorenyl)
 hafnium dimethyl, and the additional mono- and biscyclopentadienyl compounds such as
 20 those listed and described in U.S. patents 5,017,714, 5,324,800 and EP-A-0 591 756. All
 documents are incorporated by reference for purposes of U.S. patent practice.

Representative traditional Ziegler-Natta transition metal compounds include
 tetrabenzyl zirconium, tetra bis(trimethylsilylmethyl) zirconium,
 25 oxotris(trimethylsilylmethyl) vanadium, tetrabenzyl hafnium, tetrabenzyl titanium,
 bis(hexamethyl disilazido)dimethyl titanium, tris(trimethyl silyl methyl) niobium
 dichloride, tris(trimethylsilylmethyl) tantalum dichloride. The important features of such
 compositions for coordination polymerization are the ligand capable of abstraction and
 that ligand into which the ethene (olefinic) group can be inserted. These features enable

the abstraction of the transition metal compound and the concomitant formation of the ionic catalyst composition of the invention.

Additional organometallic transition metal compounds suitable as olefin
5 polymerization catalysts in accordance with the invention will be any of those Group 3-10
that can be converted by ligand abstraction into a catalytically active cation and stabilized
in that active electronic state by a noncoordinating or weakly coordinating anion
sufficiently labile to be displaced by an olefinically unsaturated monomer such as
ethylene. Exemplary compounds include those described in the patent literature. U.S.
10 patent 5,318,935 describes bridged and unbridged bisamido transition metal catalyst
compounds of Group 4 metals capable of insertion polymerization of α -olefins.
International patent publication WO 96/23010 describes diimine nickel and palladium
compounds suitable for ionic activation and olefin polymerization. Transition metal
polymerization catalyst systems from Group 5-10 metals wherein the active transition
15 metal center is in a high oxidation state and stabilized by low coordination number
polyanionic ancillary ligand systems are described in US patent 5,502,124 and its
divisional US patent 5,504,049. Bridged bis(arylamido) Group 4 compounds for olefin
polymerization are described by D. H. McConville, *et al*, in *Organometallics* 1995, 14,
5478-5480. Synthesis methods and compound characterization are presented. Further
20 work appearing in D. H. McConville, *et al*, *Macromolecules* 1996, 29, 5241-5243,
described the bridged bis(arylamido) Group 4 compounds are active catalysts for
polymerization of 1-hexene. Additional transition metal compounds suitable in
accordance with the invention include those described in co-pending U.S. patent
applications Ser. No. 08/798,401 filed 7 February 1997, Ser. No. 08/803,687 filed 24
25 February 1997, Ser. No. 08/806,181 filed 25 February 1997, Ser. No. 60/041258 filed 17
March 1997, and WO 96/40806. Each of these documents is incorporated by reference
for the purposes of U.S. patent practice.

When using the supported ionic catalysts of the invention, the total catalyst system
30 can additionally comprise one or more scavenging compounds. The term "scavenging

compounds" is meant to include those compounds effective for removing polar impurities from the reaction environment. Impurities can be inadvertently introduced with any of the polymerization reaction components, particularly with solvent, monomer and catalyst feed, and adversely affect catalyst activity and stability. Impurities can result in decreased, variable or even elimination of catalytic activity. The polar impurities, or catalyst poisons include water, oxygen, metal impurities, etc. Preferably steps are taken before provision of such into the reaction vessel, for example by chemical treatment or careful separation techniques after or during the synthesis or preparation of the various components; some minor amounts of scavenging compound can still normally be used in the polymerization process itself.

Typically the scavenging compound will be an organometallic compound such as the Group 13 organometallic compounds of U.S. patents 5,153,157, 5,241,025 and WO-A-93/14132, WO-A-94/07927, and that of WO-A-95/07941. Exemplary compounds include triethyl aluminum, triethyl borane, triisobutyl aluminum, methylalumoxane, isobutyl aluminoxane, and tri(n-octyl)aluminum. Those scavenging compounds having C₃-C₁₂ bulky, or C₈-C₂₀ linear, hydrocarbyl substituents covalently bound to the metal or metalloid center are preferred to minimize adverse interaction with the active catalyst. The amount of scavenging agent to be used with supported transition-metal cation-non-coordinating anion pairs is minimized during polymerization reactions to that amount effective to enhance activity.

Gas phase processes use supported catalysts and are conducted under gas phase conditions suitable for ethylene homopolymers or copolymers prepared by coordination polymerization. Illustrative examples may be found in U.S. patents 4,543,399, 4,588,790, 5,028,670, 5,352,749, 5,382,638, 5,405,922, 5,422,999, 5,436,304, 5,453,471, and 5,463,999, and International applications WO 94/28032, WO 95/07942 and WO 96/00245. Each is incorporated by reference for purposes of U.S. patent practice. Typically the processes are conducted at temperatures of from about -100 °C to 150 °C, preferably from about 40 °C to 120°C, at pressures up to about 7000 kPa, typically from

about 690 kPa to 2415 kPa. Continuous processes using fluidized beds and recycle streams as the fluidizing medium are preferred.

Slurry polymerization processes in which the immobilized catalyst systems of this invention may be used are typically described as those in which the polymerization medium can be either a liquid monomer, like propylene, or a hydrocarbon solvent or diluent, advantageously aliphatic paraffin such as propane, isobutane, hexane, heptane, cyclohexane, etc. or an aromatic one such as toluene. The polymerization temperatures may be those considered low, e.g., less than 50 °C, preferably 0 °C - 30 °C, or may be in a higher range, such as up to about 150 °C, preferably from 50 °C up to about 80 °C, or at any ranges between the end points indicated. Pressures can vary from about 100 to about 700 psia (0.76-4.8 Mpa). Additional description is given in U.S. patents 5,274,056 and 4,182,810 and WO 94/21962 which are incorporated by reference for purposes of U.S. patent practice.

In the process manner discussed above with the invention catalysts described in this application, unsaturated monomers, that is olefinically or ethylenically unsaturated monomers, may be polymerized so as to form polymer products having molecular weights (weight-average or M_w) from about 500 to about 3×10^6 . Most typically, the polymer products will have an M_w of from about 1000 to about 1.0×10^6 . Suitable olefinically unsaturated monomers include ethylene, C_3 - C_{20} linear or branched α -olefins, C_4 - C_{20} cyclic olefins, C_4 - C_{20} non-conjugated diolefins, C_4 - C_{20} geminally disubstituted olefins, C_8 - C_{20} styrenic olefins or C_{20} - C_{1000} α -olefin macromers. Preferably the polymer products will be any of polyethylene homopolymers and copolymers, particularly, polyethylene plastics, plastomers and elastomers; polypropylene homopolymers and copolymers, including atactic, syndiotactic or isotactic polypropylene; and cyclic olefin copolymers, particularly ethylene-norbornene copolymers.

INDUSTRIAL APPLICABILITY

The supported catalyst according to the invention will be useful for industrial means of preparing addition or insertion polymers derived from olefinically unsaturated monomers. In particular the invention catalysts will be particularly suitable for use in gas phase or slurry processes, such as those practiced industrially worldwide, largely in accordance with the description above of these processes. Such polymer manufacturing processes are responsible for large amounts of plastic, thermoplastic elastomers and elastomers for films, fibers, packaging, adhesive substrates and molded articles in common use. Additionally the methodology of the invention can be readily extended to exploit combinatorial methods of catalyst evaluation. The polymeric supported activators are valuable intermediates for the construction and screening of libraries useful for optimization of new single-site catalyst systems capable of activation by ligand abstraction.

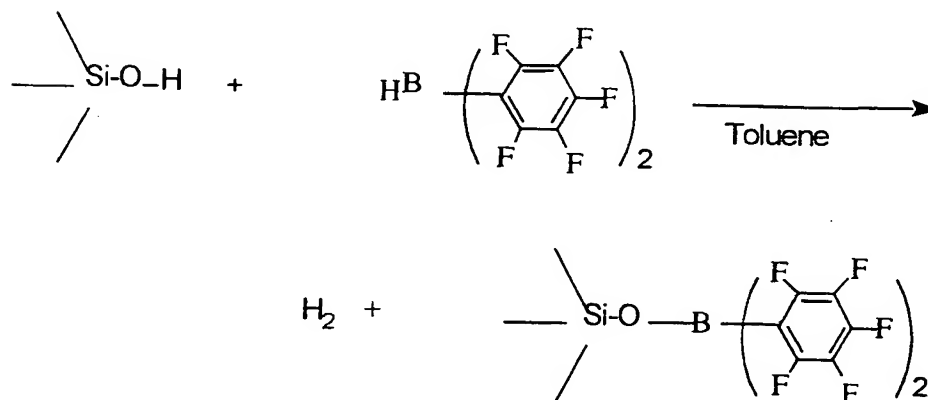
EXAMPLES

Example 1-Preparation of a Silica Bound Lewis Acid A

1.00 g of silica (Davison 948, dried at 600° C) was suspended in anhydrous toluene at 25° C under an atmosphere of nitrogen (glove box). To this slurry was added a toluene solution containing 0.123 g of $\text{HB}(\text{C}_6\text{F}_5)_2$. Gas evolution was observed immediately after the addition of the borane solution. Although no physical/chemical analyses have been conducted, it is likely that this gas is hydrogen. The slurry was allowed to stir for 1 hour. After this period the white solid was collected by vacuum filtration, washed two times with 5 ml portions of dry toluene, and allowed to dry under reduced pressure for 30 minutes. See the chemical reaction sequence represented below.

Example 2-Preparation of a Silica Bound Lewis Acid B

5.89 g of silica (Davison 948, dried at 800° C) was suspended in anhydrous toluene at 25° C under an atmosphere of nitrogen (glove box). To this slurry was added a toluene solution containing 0.707 g of HB(C₆F₅)₂. Gas evolution was observed immediately after the addition of the borane solution. Although no physical/chemical analyses have been conducted, it is likely that this gas is hydrogen. The slurry was allowed to stir for 1 hour. After this period the white solid was collected by vacuum filtration, washed two times with 10 ml portions of toluene, and allowed to dry under reduced pressure for 30 minutes. The following representation illustrates this reaction.

**Example 3-Catalyst A Preparation**

A yellow toluene solution containing 24 mg of (CH₃)₂Si(2-methyl-4-phenylindene)Zr(CH₃)₂ was added to a slurry containing 0.100 g of the Silica Bound Lewis Acid A (*vide supra*). A yellow to orange color change was observed immediately after the solution containing the transition metal compound was added to the slurry of the Silica Bound Lewis Acid A. In this connection, it is important to notice that this is the

same color change observed when $(\text{CH}_3)_2\text{Si}(2\text{-methyl-4-phenylindene})\text{Zr}(\text{CH}_3)_2$ is activated with similar discrete activators (e.g. $\text{B}(\text{C}_6\text{F}_5)_3$ or $[(\text{C}_6\text{H}_5)\text{NH}(\text{CH}_3)_2][\text{B}(\text{C}_6\text{F}_5)_4]$). After stirring for 30 minutes the orange solid was collected by vacuum filtration, washed with two 5 ml portions of dry toluene, and dried under reduced pressure for 20 minutes.

Example 4-Catalyst B Preparation

A yellow toluene solution containing 31 mg of $(\text{CH}_3)_2\text{Si}(2\text{-methylindene})\text{Hf}(\text{CH}_3)_2$ was added to a slurry containing 0.100 g of the Silica Bound Lewis Acid A (*vide supra*). A slight color intensification (pale yellow to bright yellow) was observed immediately after the solution containing the transition metal compound was added to the slurry of the Silica Bound Lewis Acid A. After stirring for 30 minutes the bright yellow solid was collected by vacuum filtration, washed with two 5 ml portions of dry toluene, and dried under reduced pressure for 20 minutes.

Example 5-Slurry-Phase Propylene Polymerization

The polymerization described below was carried out in a 1-liter autoclave reactor equipped with a mechanical stirrer, an external water-steam jacket for temperature control, two inlet ports for catalyst or scavenger delivery, and pressure controlled supply of propylene or nitrogen. Prior to the polymerization reaction the reactor was dried by heating the reactor body to 110° C for 30 minutes under a constant nitrogen purge. This procedure allows for degassing the reactor as well. Into the reactor was added 200 ml of dry toluene, 1.0 ml of a 10 wt% triisobutylaluminum solution (toluene), and 100 ml of propylene. The reactor was brought to 70° C. A 50 mg portion of Catalysts A described in example 3 was pressurized into the reactor with 100 ml of pressurized propylene. A slight exotherm (2° C) was observed immediately after the catalyst was added to the reactor. The temperature of the reactor was maintained at 70° C. After 10 minutes of reaction time the temperature was reduced to 30° C and the pressure in the reactor was removed by ventilation. The polymer was collected and thoroughly dried for 24 hours in

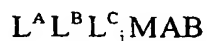
a vacuum oven kept at 50° C. 10.6 g of polypropylene was obtained after drying. Gas permeation chromatography (GPC) was used to characterized the resulting polymer. The number average molecular weight was 297,000, the weight average molecular weight was 553,000, and the polydispersity index ("PDI") or molecular weight distribution was 1.86.

Example 6-Liquid Propylene Polymerization (bulk)

The polymerization described below was carried out in a 1-liter autoclave reactor equipped with a mechanical stirrer, an external water-steam jacket for temperature control, two inlet ports for catalyst or scavenger delivery, and pressure controlled supply of propylene or nitrogen. Prior to the polymerization reaction the reactor was dried by heating the reactor body to 110° C for 30 minutes under a constant nitrogen purge. Into the reactor was added 1.0 ml of a 10 wt% triisobutylaluminum solution (toluene), and 200 ml of propylene. The reactor was brought to 70° C. A 50 mg portion of Catalysts B described in example 4 was pressurized into the reactor with 200 ml of pressurized propylene. A slight exotherm (1° C) was observed immediately after the catalyst was added. The temperature of the reactor was maintained at 70° C. After 30 minutes of reaction time the temperature was reduced to 30° C and the pressure in the reactor was removed by ventilation. The polymer was collected as a wet solid and dried for 24 hours in a vacuum oven kept at 50° C. 5.9 g of polypropylene was obtained after drying. Gas permeation chromatography (GPC) was used to characterized the resulting polymer. The number average molecular weight was 266,000, the weight average molecular weight was 479,000, and the PDI was 1.80.

CLAIMS:

1. An olefin polymerization catalyst which is the reaction product of 1) transition metal compounds having ancillary, stabilizing ligands and at least two labile ligands suitable for insertion of olefins and capable of abstraction or removal so as to form active cationic transition metal centers and 2) a support bound, neutral Lewis acid comprising a boron atom having two halogenated aryl ligands and a third ligand being a heteroatom covalently bonded to a polymeric or metal/metalloid oxide support.
2. The catalyst composition of claim 1 wherein said heteroatom is a Group 15 or 16 heteroatom.
3. The catalyst composition of claim 1 or 2 wherein said halogenated aryl ligands are perfluorinated phenyl, naphthyl, anthracenyl, or biphenyl ligands.
4. The catalyst composition of any of claims 1-3 wherein said transition metal compounds are selected from the group consisting of Group 3-10 transition metal compounds capable of activation for olefin polymerization by ligand abstraction.
5. The catalyst composition of claim 4 wherein said transition metal organometallic catalyst compound is a Group 4 metallocene compound having the formula:



where, L^A is a substituted or unsubstituted cyclopentadienyl or heterocyclopentadienyl ancillary ligand π -bonded to M; L^B is a member of the class of ancillary ligands defined for L^A , or is J, a heteroatom ancillary ligand σ -bonded to M; the L^A and L^B ligands may be covalently bridged together through a Group 14 element linking group; L^C_i is an optional neutral, non-oxidizing ligand

having a dative bond to M (i equals 0 to 3); M is a Group 4 transition metal; and, A and B are independently monoanionic labile ligands, each having a σ -bond to M, optionally bridged to each other or L^A or L^B , which can be broken for abstraction purposes by a suitable activator and into which a polymerizable monomer or macromonomer can insert for coordination polymerization.

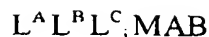
6. The catalyst composition of claim 5 wherein M is titanium and L^B is J, a heteroatom ancillary ligand σ -bonded to M.

7. The catalyst composition of claim 5 wherein M is zirconium or hafnium and L^B is independently a substituted or unsubstituted cyclopentadienyl or heterocyclopentadienyl ancillary ligand π -bonded to M.

8. A process for the polymerization of olefinically unsaturated monomers comprising contacting a plurality of one or more of said monomers with an olefin polymerization catalyst which is the reaction product of 1) transition metal compounds having ancillary, stabilizing ligands and at least two labile ligands suitable for insertion of olefins and capable of abstraction or removal so as to form active cationic transition metal centers and 2) a support bound Lewis acid comprising a boron atom having two halogenated aryl ligands and a third ligand being a heteroatom covalently bonded to a polymeric or metal/metalloid oxide support.

9. The process of claim 8 wherein said transition metal compound is a Group 3-10 transition metal compound capable of activation for olefin polymerization by ligand abstraction.

10. The process of claim 8 or 9 wherein said transition metal compound is a Group 4 metallocene compound having the formula:



where, L^A is a substituted or unsubstituted cyclopentadienyl or heterocyclopentadienyl ancillary ligand π -bonded to M; L^B is a member of the class of ancillary ligands defined for L^A , or is J, a heteroatom ancillary ligand σ -bonded to M; the L^A and L^B ligands may be covalently bridged together through a Group 14 element linking group; L^C_i is an optional neutral, non-oxidizing ligand having a dative bond to M (i equals 0 to 3); M is a Group 4 transition metal; and, A and B are independently monoanionic labile ligands, each having a σ -bond to M, optionally bridged to each other or L^A or L^B , which can be broken for abstraction purposes by a suitable activator and into which a polymerizable monomer or macromonomer can insert for coordination polymerization.

11. The process of any of claims 8-10 wherein said olefin polymerization conditions comprise a solution, supercritical pressure, bulk, slurry or gas phase process conducted at reaction temperatures between -20 °C - 200 °C and pressures between 0 - 2000 bar.
12. The process of claim 10 wherein said process is bulk, slurry or gas phase.
13. The process of claim 12 wherein said olefinically unsaturated monomers are selected from the group consisting of ethylene and one or more of C_3 - C_8 α -olefins, C_6 - C_{20} diolefins, styrene or alkyl-substituted styrene, and C_5 - C_{20} cyclic olefins.
14. The process of claim 11 wherein said olefinically unsaturated monomers are selected from the group consisting of propylene and, optionally, one or more of C_2 - C_8 α -olefins, and C_6 - C_{20} diolefins.

15. The process of any of claims 8-14 wherein said heteroatom is oxygen and said support comprises silica.
16. The process of any of claims 8-14 wherein said heteroatom is oxygen or nitrogen and said support is polymeric.

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/15733

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F4/603 C08F4/02 C08F10/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>EP 0 824 112 A (HOECHST AG) 18 February 1998 (1998-02-18) claims 1-3 page 6, line 27 - line 35 page 6, line 46 - line 48 page 7, line 23 -page 8, line 54 page 9, line 41 - line 48 page 17, line 47 page 19, line 25 - line 31 examples 10,13,16</p> <p style="text-align: center;">--- -/--</p>	1-16

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

13 October 1999

Date of mailing of the international search report

03/11/1999

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/15733

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	<p>TIAN, JUN ET AL: "Borane-functionalized oxide supports: development of active supported metallocene catalysts at low aluminoxane loading"</p> <p>J. MOL. CATAL. A: CHEM. (1999), 144(1), 137-150 , XP002118632</p> <p>page 138, Eq (2)</p> <p>page 138, paragraph 5 -page 143, paragraph 2</p> <p style="text-align: center;">-----</p>	<p>1-5, 7-13,15</p>

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/15733

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0824112 A	18-02-1998	DE 19632557 A	19-02-1998
		DE 19632558 A	19-02-1998
		DE 19647070 A	20-05-1998
		AU 3413397 A	19-02-1998
		BR 9704310 A	15-06-1999
		BR 9704354 A	12-01-1999
		CA 2212668 A	13-02-1998
		CN 1182093 A	20-05-1998
		CN 1174205 A	25-02-1998
		EP 0824113 A	18-02-1998
		JP 10139806 A	26-05-1998
		JP 10158269 A	16-06-1998
		NO 973707 A	16-02-1998

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